

Ground state, electronic structure and magnetism of LaMnO₃

R.J. Radwanski*

Center for Solid State Physics, S^{nt}Filip 5, 31-150 Krakow, Poland,

Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

Z. Ropka

Center for Solid State Physics, S^{nt}Filip 5, 31-150 Krakow, Poland

We have calculated the discrete low-energy electronic structure in LaMnO₃ originating from the atomic-like states of the strongly correlated 3d⁴ electronic system occurring in the Mn³⁺ ion. We take into account very strong intra-atomic correlations, crystal field interactions and the intra-atomic spin-orbit coupling. We calculated magnetic and paramagnetic state of LaMnO₃ within the consistent description given by Quantum Atomistic Solid State Theory (QUASST). Our studies indicate that the intra-atomic spin-orbit coupling and the orbital magnetism are indispensable for the physically adequate description of electronic and magnetic properties of LaMnO₃.

Keywords: 3d oxides, crystal field, spin-orbit coupling, LaMnO₃

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The present study is a continuation of our systematic investigations on the electronic structure and magnetic properties of compounds containing transition-metal atoms. Problem of the Mn³⁺ ion containing compounds is of particular interest. LaMnO₃ is an insulating antiferromagnet with the Neel temperature of 140 K [1, 2, 3, 4]. Recently in LaMnO₃ the problem of the orbital ordering is widely discussed. The orbital ordering appears much above Neel temperature. For us the orbital ordering is related to local distortions well accounted in terms of crystal-field interactions. It is a reason for our

long lasting studies of crystal-field interactions in 3d-/4f-/5f-atom containing compounds. The Mn ions in the perovskite structure sit in the distorted oxygen octahedron. The basis for all theories is the description of the Mn³⁺ ion and its electronic structure. There is no consensus about the description of this electronic structure.

The aim of this paper is to present a consistent description of the low-energy electronic structure and of the magnetism of LaMnO₃. In our understanding, formulated as the Quantum Atomistic Solid State Theory (QUASST) [5, 6], the low-energy electronic structure is related to the atomic-like electronic structure of the strongly-correlated 3d⁴ electronic system occurring in the Mn³⁺ ion. In our description

*URL: <http://www.css-physics.edu.pl>; Electronic address: sfradwan@cyf-kr.edu.pl

the orbital magnetism and the intra-atomic spin-orbit coupling play the fundamentally important role.

The four d electrons of the Mn^{3+} ion in the incomplete $3d$ shell in LaMnO_3 form the strongly correlated intra-atomic $3d^4$ electron system. These strong correlations among the $3d$ electrons we account for by two Hund's rules, that yield the 5D ground term, Fig. 1a. In the oxygen octahedron surroundings, realized in the perovskite structure of LaMnO_3 , the 5D term splits into the orbital doublet 5E_g as the ground subterm, Fig. 1b, and the excited orbital triplet $^5T_{2g}$. For physically adequate description of states we have to take into account the intra-atomic spin-orbit coupling because it is always present in the ion.

The E_g ground subterm comes out from *ab initio* calculations for the octupolar potential, the A_4 CEF coefficient acting on the Mn^{3+} ion from the oxygen negative charges. Such the atomic-like $3d^4$ system interacts with the charge and spin surroundings in the solid. The interaction with the charge surroundings we approximate by means of the crystal-field interactions. As is shown in Fig. 1c, the energy level scheme of the $3d^4$ system in the octahedral crystal field and in the presence of the spin-orbit coupling contains 25 states in the spin-orbital space. The dominating octahedral crystal field leaves 10 lowest states well separated from others. These 10 states are split in two quintets by the tetragonal distortion, see Fig. 1d. The splitting of two

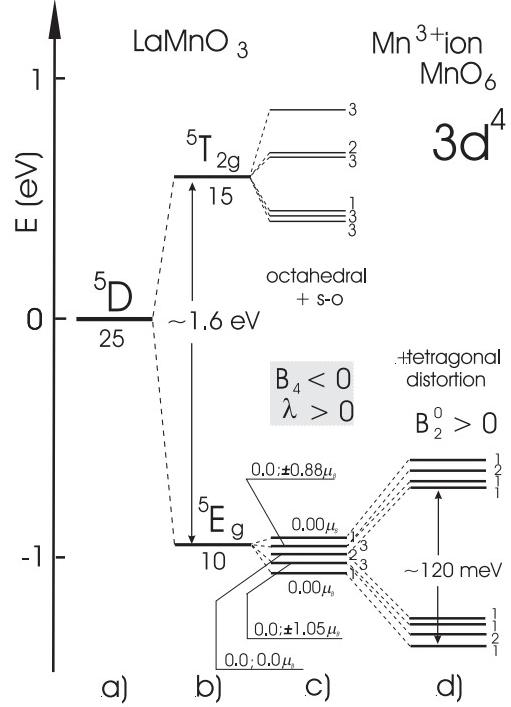


FIG. 1: Calculated electronic structure of the lowest 5D term (a) of the $3d^4$ electronic system occurring in the Mn^{3+} ion realized in LaMnO_3 , produced by the octahedral crystal field (b), the intra-atomic spin-orbit coupling (c) and the tetragonal distortion (d). The degeneracy and the magnetic moment of the states are shown. The fine splitting is not to the left-hand scale.

quintets is of order of 120 meV and we think that this splitting has been revealed in Raman spectra [7]. This fine electronic structure predominantly governs the electronic and magnetic properties of real $3d$ -ion systems. To such electronic structure we superimpose the spin-dependent interactions to account for the macroscopically observed magnetic state. The appearance of the magnetic state is associated with the spin polarization and the temperature dependence of the

energy of the levels as is seen in Fig. 2. The self-consistent calculations have been performed similarly to that presented in Ref. [8] for FeBr_2 . With the octahedral CEF parameter $B_4 = -13$ meV, $B_2^0 = +10$ meV, the spin-orbit coupling parameter $\lambda_{s-o} = +33$ meV and the molecular-field coefficient $n = 26.3 \text{ T}/\mu_B$ we get a value of $3.72 \mu_B$ for the Mn^{3+} -ion ordered magnetic moment. This value is in good agreement with the experimental datum. LaMnO_3 has been calculated to order magnetically along the a axis within the tetragonal plane. The magnetic interactions set up at 0 K the molecular field of 108 T. The calculated magnetic moment of $3.72 \mu_B$ is built up from the spin moment of $+3.96 \mu_B$ and from the orbital moment of $-0.24 \mu_B$. Although the orbital moment is relatively small its presence modifies completely the electronic structure. The Mn^{3+} ground-state wave function is given as $\psi = 0.87|x^2 - y^2, -2\rangle + 0.48|z^2, -2\rangle$. Having the electronic structure, both in the magnetic and paramagnetic state, we can calculate the free Helmholtz energy and the resulting thermodynamical properties by means of the statistical physics.

The calculated electronic structure differs fundamentally from those presented in the current literature [1, 2, 3, 4] with t_{2g} and e_g one-electron orbitals. In contrary to the one-electron description used in presently-in-fashion theories we work with many-electron functions of $S=2$ and $L=2$. In case of the Mn^{3+} ion, its four d electrons are put in literature subsequently

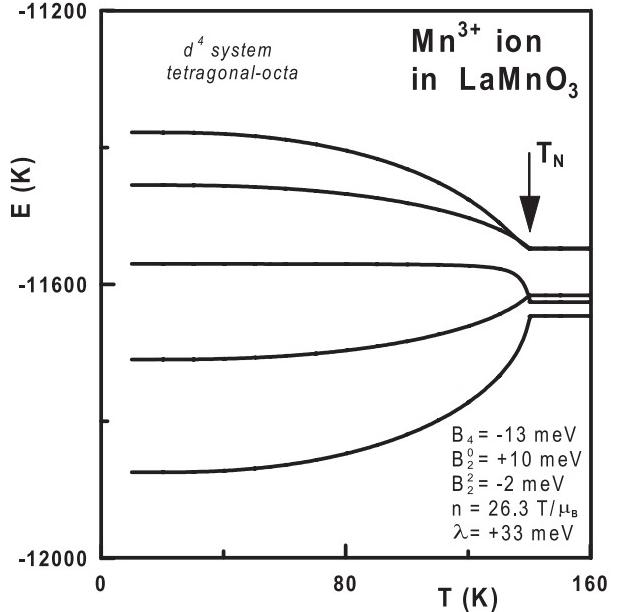


FIG. 2: Calculated temperature dependence of the energy of the 5 lowest levels of the Mn^{3+} ion in LaMnO_3 in the paramagnetic ($T > T_N = 140 \text{ K}$) and the magnetic ($T < T_N$) state with the magnetic moments along the a axis. Parameters are in the figure.

on the t_{2g} (three electrons with spin up) and e_g (the fourth electron) orbitals. Such the picture we consider as completely oversimplified - it neglects mutual interactions within the incomplete 3d shell. In contrast, our approach is the crystal-field approach with strong electron correlations and with the importance of the spin-orbit coupling. Comparison of different theoretical approaches, the band theory, the one electron crystal-field approach and our many-electron crystal-field theory has been presented in Ref. [9]. We are surprised that the presented by us many-electron crystal-field approach is not popular among the 3d theoretists though it was Van Vleck who already in a year of 1935, i.e. seventy

years ago, has shown its substantial applicability to iron-group compounds [10]. We continue the research by Van Vleck by taking into account the spin-orbit coupling and by calculating *explicitely*, not by a perturbation method, the eigenstates and eigenfunctions of the 3d paramagnetic ions in the Hund's rules ground terms in a solid [11]. Moreover, we manage to combine the CEF theory with spin-dependent interactions, for Hamiltonian see to Ref. [8] - the same was used here for getting Fig. 2, that enables to calculate the magnetically-ordered state within one consistent procedure. Having eigenstates and eigenfunctions all thermodynamics can be calculated. It means, that properties like temperature dependence of the magnetic moment, of the paramagnetic susceptibility and of the heat capacity can be calculated from *first principles*. Thus we were extremely surprised that our paper showing a scheme similar to that shown in Fig. 1 has been rejected by the Organizing Committee of Strongly-Correlated Electron Conference in 2002, because for the Committee and its referees it was unclear why the derived by us the level structure with the E_g ground state "is reversed with respect to the t_{2g} - e_g structure obtained by many authors" [12]. We could not believe that within the Organizing Committee (and also within the International Committee as we have asked to inform them about our protest) there was no one who could understand our long explanations that the E_g ground state comes out from *ab initio* CEF calculations for the Mn^{3+} ion in

the oxygen octahedron. Such a rejection reveals the enormous shortage of knowledge about the CEF theory - orbitals are not distinguished from the state symmetry. This difference is clearly defined in text-books of Abragam and Bleaney [13], Ballhausen [14], and many, many others. This shortage of knowledge about the crystal field we met earlier in Phys. Rev. B and Phys. Rev. Lett. Our papers from 1996 explaining properties of LaMnO_3 with the E_g ground state of the Mn^{3+} ion in LaMnO_3 (BZR586, BER639, LA6567 - it can be found as Ref. [15]) and pointing out the importance of the spin-orbit coupling has been rejected as having an incorrect ground state. Moreover, the referee wrote that our program must be wrong as it splits the E_g state. Although we could persuade the referee that our program calculates well the splitting of the E_g state, the Editors have maintained the rejection. Thus, we collect very large evidence for the discrimination of the crystal-field approach with the spin-orbit coupling among the solid-state community. It prohibits the open scientific discussion about the magnetism and the electronic structure of 3d-atom containing compounds. We are convinced, however, that the scientific truth will finally come up. We claim that the spin-orbit coupling and strong intraatomic electron-correlations have to be taken into account for the physically adequate description. It is the highest time to "unquench" the orbital moment in the 3d solid-state physics.

In conclusion, we argue that in LaMnO_3 there

is preserved low-energy electronic structure originating from atomic-like states of the strongly correlated $3d^4$ electronic system occurring in the Mn^{3+} ion. Our approach provides a microscopic mechanism for the electron-lattice and the spin-lattice coupling as well as for the electron-electron correlations. We are convinced that the orbital degree of freedom (L) and the intraatomic spin-orbit coupling are indispensable for the physically adequate description of electronic and magnetic properties of $LaMnO_3$. A discrete atomic-like electronic structure in the meV scale has been revealed recently in $LaCoO_3$ [16, 17] confirming the basic assumption of the devel-

oped by us Quantum Atomistic Solid State Theory. QUASST enables calculations of the value and the direction of the local magnetic moment and reveals that they are predominantly governed by the local lattice symmetry. We get a value of $3.72 \mu_B$ for the Mn^{3+} ion magnetic moment - this value depends on local distortions and contains the substantial orbital moment. Our approach accounts for the insulating state as well as for a number of transitions observed in the Raman-scattering experiment on $LaMnO_3$ and provides the proper symmetry of the ground state eigenfunction.

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